phenylhydrazones for determining carbonyl concentrations in essence. Braddock and Petrus (1971A,B) determined the malonaldehyde content of citrus essences by treating them with thiobarbituric acid to form a pink complex that was quantitated by measuring the fluorescence and phosphorescence spectra. They related the malonaldehyde content to essence quality and suggested the former as an index of flavor quality in citrus essences.

Moshonas and Lund (1971) developed a gas chromatographic procedure for separating the total organics (those other than the three main organic components, ethanol, methanol and acetaldehyde) in essence for further detailed analysis. Moshonas and Shaw (1975) used this method, as well as a bromate titration method, to determine relative strength of different essences prepared from the same essence recovery unit. Veldhuis *et al.* (1972) extracted essence by the methylene chloride procedure of Wolford *et al.* (1962) and determined organic components other than methanol, ethanol and acetaldehyde either gravimetrically or by quantitative gas chromatography. Randall *et al.* (1973) pointed out that the disadvantages of the methylene chloride extraction procedure for quantitative work were incomplete essence extraction, losses of some components upon concentration of the methylene chloride extract, and the time consuming and sometimes inexact integration of peak areas in gas chromatograms. They used ultraviolet absorption of essence as a measure of strength, which they then correlated with the value from the bromate titration method of Moshonas and Shaw (1975).

Despite the variety of attempts to correlate either essence strength or flavor acceptance with analytical measurement, no one objective test has been found either to replace or to equal organoleptic evaluation of essence. Tasting essence either in orange juice or in aqueous sugar-acid-pectin mixtures (Braddock and Petrus 1971B) is still the method of choice for judging quality and strength of essences to be sold commercially.

Quantitative analysis of individual compounds in orange essence has received little attention compared to qualitative analysis or to quantitative analysis of compound classes. Hall and Wilson (1925) determined the ethanol content of fresh Valencia orange juice to be about 0.018% by analyzing essence prepared on laboratory scale. Kirchner and Miller (1957) quantitated ethanol, acetaldehyde, methanol, acetic acid and a partially characterized acid in essences from fresh, freshly canned and stored canned juices of Valencia orange. They reported more ethanol (0.04%) in fresh juice than Hall and Wilson had found. Moshonas and Lund (1971) described a rapid gas chromatographic method for determining ethanol, methanol and acetaldehyde content in citrus essences, and reported a value of 10.4% ethanol for the orange essence analyzed. Shaw and Moshonas (1974) reported the percentages of water (10.8), acetaldehyde (0.9), methanol (3.2), ethanol (84.5), ethyl acetate (0.5) and limonene (0.2) present in a concentrated orange essence. Swift (1961) reported the levels of linalool and α-terpineol (0.3 to 2.3 and 0.6 to 1.1 mg per l of juice) found in a distillate from freshly canned orange juice. Moshonas and Shaw (1973) estimated the concentration of *trans*-2-pentenal as 750 ppb in orange essence by gas chromatographic analysis of a methylene chloride extract from essence. No systematic quantitative study of individual compounds in orange or any other citrus essence has been reported.

Flavor Significance and Stability

Use of essence to enhance the flavor of frozen concentrated orange juice (FCOJ) has increased to the point that some 25 to 50% of the FCOJ produced in Florida now contains added essence (Dougherty *et al.* 1974). Commercial essence is usually described as hundred-fold, that is, one part flavors per 100 parts single-strength orange juice. Essence imparts a fresh orange flavor, or bouquet, to the flavor of processed juice. It compliments or even replaces the use of fresh cut-back juice, which adds fresh flavor to FCOJ (Veldhuis 1971). Dougherty *et al.* (1974) studied the effects of various levels of essence on orange juice flavor and concluded that in juice there is an optimum level for essence and that higher levels than this decrease flavor quality. They also showed that essence-enhanced FCOJ retained acceptable essence flavor for periods of up to 30 months frozen storage. This finding contrasts with the widely accepted belief that FCOJ containing essence tends to lose its essence-like flavor during storage. Guadagni *et al.* (1970) showed that samples of orange essence were unstable even at –18°C unless stored in the dark in sealed containers. They showed that *d*-limonene decreased during storage deterioration of essence, and that exclusion of air and light were both more important to essence flavor stability than storage temperature (up to 21°C). Askar *et al.* (1973) studied changes in volatile constituents of essence-containing orange juice stored for up to six months at room temperature. They found levels of limonene and linalool decreased during storage while levels of α-terpineol and decanal increased. Hexanal, hexenal and octanal levels increased during the first two months of storage, then began to decrease. They proposed α-terpineol as an indicator of storage history for orange juice.

The importance of several essence constituents to orange juice flavor has been reported. Moshonas and Shaw (1973) suggested the

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trace components 1-penten-3-one (ethyl vinyl ketone) and *trans*-2-pentenal to be important to essence flavor, the former because of its penetrating acetylene-type aroma and the latter because of its fruity or apple-like aroma and astringent taste at near threshold concentration. Dougherty and Ahmed (1973) determined odor and flavor thresholds of selected components of orange essence in water. They also tested some of these compounds singly or in combination for their positive or negative contribution to the flavor of orange juice prepared from evaporator pumpout (orange concentrate containing no added oil, cut-back juice or essence). The flavors of these preparations were compared with a control juice prepared from a good quality concentrate of orange juice containing orange oil, cut-back juice, and essence as flavor enhancers. Table 12.2 lists results of their studies on selected components of orange essence and shows positive or negative contributions to orange juice flavor for certain components. Levels of compounds added to juice from evaporator pumpout were chosen from values reported in the literature. Generally juice containing combinations of several components received higher sensory ratings (data not shown) than did those containing single compounds.

Concentrated Essence

The commercial hundred-fold essence of today contains ethanol at an upper limit of about 15% so that no alcohol tax has to be paid on the product. Since demand for essence has increased in other parts of the world, a more concentrated solution of flavor organics would be a desirable product to market. Its storage and shipping costs would decrease and its storage stability would increase. Shaw and Moshonas

TABLE 12.2

FLAVOR EVALUATION OF SELECTED ORANGE ESSENCE COMPONENTS

Compound	Flavor Threshold in Water (ppb)	Level Tested in Juice	Contribution to Orange Flavor
Acetaldehyde	20	3000	+
Butanal	5		N[1]
Ethanol	10,000		N
Ethyl butyrate	0.125	400	+
Ethyl propionate	7.6		N
trans-2-Hexenal	50	9000	-
Methyl butyrate	60		N
Octanal	0.5	60	+
1-Penten-3-one	1.2	100	-

[1] Not determined.

(1974) analyzed a commercially prepared concentrate of essence and showed it to be about 85% ethanol. The other major organic components were present in about the same proportion as that found in hundred-fold essence. Concentrated essence has recently been judged by the Federal Bureau of Alcohol, Tobacco and Firearms to be naturally denatured and, as such, not subject to an alcohol tax. This product will probably gain increasing worldwide acceptance. Thus, the demand for orange and other citrus essences in this concentrated form may increase.

Aroma Solutions

Veldhuis *et al.* (1972) found that aqueous solutions of volatile orange constituents (aroma solutions) could be distilled from aqueous slurries of ground whole peel, flavedo, albedo, from peel-oil-free juice (juice from oranges peeled prior to extraction) or from centrifuge effluent (the aqueous discharge from peel oil centrifugation). Such aqueous solutions were shown by Moshonas *et al.* (1972) to contain many of the components found in essence. Lund *et al.* (1972) showed quantitative variations in aroma solutions from centrifuge effluents as processing conditions were varied. Most of these aroma solutions are produced from what are normally regarded as waste products in a citrus plant. In the case of centrifuge effluent, removal of an aroma solution actually aids in purification of this waste stream. Some of the aroma solutions have flavor properties similar to those of commercial essence (Berry and Wagner 1974).

GRAPEFRUIT, TANGERINE, LEMON AND LIME ESSENCES

In preparing a concentrated juice product from grapefruit, tangerine, lemon or lime, an essence recovery unit can be operated to afford essence having a fresh-fruit aroma. The essence of lemon or lime is strongly characteristic of the fruit. Perhaps the least desirable citrus essence for flavoring is that from tangerine. It has an undesirable "fishy" aroma that disappears upon preparation of anhydrous essence (Moshonas and Shaw 1972A). Disappearance of the odor indicates that a volatile or labile component is responsible for the undesirable aroma. Analytical studies on essences of citrus other than orange have been relatively few. Kirchner *et al.* (1953) reported qualitative and quantitative measurements of seven identified and three partially characterized components of grapefruit essence prepared on laboratory scale. Moshonas and Shaw (1971, 1972A,B) reported the only analytical studies on commercial grapefruit as well as tangerine, lemon and lime essences.

TABLE 12.3

CITRUS ESSENCE COMPOSITION

Component	Grapefruit	Tangerine	Lemon	Lime
Acids				
Acetic acid	x			
Alcohols				
Borneol				x
1-Butanol	x	x	x	
cis-Carveol	x			
trans-Carveol	x		x	
Citronellol		x		
p-Cymene-8-ol				x
Ethanol	x	x	x	x
Geraniol				x
1-Hexanol	x	x	x	
cis-3-Hexen-1-ol	x	x	x	x
Linalool	x	x	x	x
trans-2,8-*p*-Menthadien-1-ol	x	x		
1,8-*p*-Menthadien-9-ol		x		
8-*p*-Menthen-1,2-diol	x			
cis-*p*-2-Menthen-1-ol			x	x
Methanol	x	x	x	x
3-Methyl-1-butanol	x	x		x
2-Methyl-2-butanol				x
2-Methyl-3-buten-2-ol		x	x	x
3-Methyl-2-buten-1-ol			x	x
2-Methyl-1-propanol	x	x		
Nerol		x	x	x
1-Octanol	x	x		
1-Penten-3-ol		x		
2-Propanol				x
Terpinen-4-ol	x	x	x	
α-Terpineol	x	x	x	
Thymol		x		
Aldehydes				
Acetaldehyde	x	x	x	x
Furfural	x			
Geranial	x		x	x
Hexanal	x	x		x
2-Hexenal	x	x		x
Neral	x		x	x
Octanal	x	x		
Perillaldehyde		x	x	x
Esters				
Ethyl acetate	x	x	x	x
Ethyl butyrate	x	x		
Ethyl 3-hydroxyhexanoate	x	x		
Methyl butyrate	x	x		
Neryl acetate				x
Hydrocarbons				
p-Cymene				x
Limonene	x	x	x	x
Myrcene			x	
γ-Terpinene			x	x
Ketones				
Acetone	x	x	x	x
Carvone	x		x	
4-Methyl-2-pentanone			x	
Nootkatone	x			
Piperitenone		x	x	x

TABLE 12.3 (*Continued*)

Component	Grapefruit	Tangerine	Lemon	Lime
Oxides				
1,8-Cineole				x
cis-Linalool oxide	x	x		x
trans-Linalool oxide	x	x		x
Miscellaneous				
1,1-Diethoxyethane	x	x		
1,4-Dioxane			x	
1,1-Ethoxymethoxyethane		x		x
Hydrogen sulfide	x			

Table 12.3 lists the compounds identified in these four citrus essences. With few exceptions the same compounds have also been found in orange essence. Most components were present in more than one of the four essences, but only eight components (ethanol, *cis*-3-hexen-l-ol, linalool, methanol, acetaldehyde, ethyl acetate, limonene and acetone) were common to all four essences.

Of the compounds reported present in citrus essences, only a few are believed important to the flavor of the fruit from which they were obtained. Nootkatone, found in grapefruit essence, is a primary flavoring compound of grapefruit (MacLeod and Buigues 1964). Thymol was isolated only from tangerine essence and is believed important to tangerine flavor (Kugler and Kovats 1963).

Neral and geranial, which are important to lemon (Ikeda *et al.* 1962) and expressed lime (Slater and Watkins 1964) flavors, were major organic components of both lemon and lime essences, but were minor organic constituents of grapefruit, tangerine and orange essences (Moshonas *et al.* 1972). 1,8-Cineole was identified only in lime essence and as a major organic component of it. This terpene ether was shown by Slater and Watkins (1964) to be a major oxygenated constituent of distilled lime oil.

Analytical studies on citrus essences have not resolved the question of what makes fresh citrus juice taste precisely the way it does. Perhaps further quantitative studies on essence composition will help to show the proportion of components needed to achieve a fresh citrus flavor. Perhaps there are important volatile citrus flavor components still unidentified. More likely, knowledge of as yet unidentified components, as well as the correct proportion of components, will answer the question of why processed citrus juices do not as yet taste exactly like the fresh juice used in preparing them.

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Inorganic Elements

The inorganic elements of citrus fruits and prod material (ash) remaining after all organic matter ha The percentage of ash and the relative concentra constituents in citrus fruits are dependent upon g (fertilization, soil type, climate, temperature a health, stock-scion relationship, cultivar, stage of m harvest and geographic origin. Likewise the perce of inorganic elements in processed products is several processing parameters; pressure used to ju of pulp and rag content (finishing), and pulp washir

Many reports on the mineral compositions of cessed citrus juices have failed to consider that levels of certain elements (e.g., sodium, phosphor these juices may have been due to processing cond to the fruit's normal mineral levels. Citrus proces periodically washed with phosphate-containing de line hydroxide solutions (mainly NaOH). Altho effort is made to remove (H_2O rinse) these deterg solutions from equipment, minor contamination o cleansing solutions is highly probable. Fruit, prior washed in a detergent solution (e.g., Fruit Cleaner rinsed in a dilute chlorinated solution. Solutions us rinsing may be of high mineral content (e.g. soc and therefore may also add to the juice's reporte

Possible contamination factors and the diverse m in mineral analyses have been taken into considerat during collection of these mineral data. The purpo will be to focus primarily upon the major inorgan Ca, Mg, Na, K, Fe, P, S, Cl and N) in fruit and juic juices have been shown by Birdsall *et al.* (1961) to tion to the major elements, the following minor mi less than 1% of the ash: Si, Mn, B, Sr and Al and '0.01% of the ash: Cu, Li, Ti, Ni, Cr, V, Bi, Zr, Pl Mo, Ag and Zn.